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## COLORIMETRIC CHARACTERISTICS OF COLORED SINGLE-COAT ENAMELS

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Compositions for single-coat glass enamels that allow obtaining a wide color range of coatings with sufficiently good surface quality for steel articles were developed. Different dyes were tested. Properties of the coatings such as the chemical stability, adhesive strength, gloss, and thermal stability were investigated and the firing temperature range, 670–740°C on average, was determined. The colorimetric characteristics of single-coat enamels were calculated. The enamel coatings obtained can be used in mass production.

The technical and economic trends in conserving natural and energy resources are now beginning to be very important.

Single-coat enameling, which allows conserving raw materials and power by reducing the coats and number of firings, is one such promising trend. The use of single-coat coatings makes it possible to obtain a higher-quality surface on the articles, since the surface becomes more elastic and shock-resistant when the resulting coating thickness decreases. The requirements (sufficiently high chemical stability, thermal stability, adhesive strength) imposed on the composition of single-coat enamels are high, since it combines the functions of primer and coating enamels. In analyzing the different published sources [1], we found that the existing single-coat glass enamels for steel are relatively high-melting, have low enough adhesive strength, and most of them are in dark colors (black, brown, dark blue, dark green). For this reason, we investigated the possibility of manufacturing an expanded color range of single-coat enamels for steel articles for household use with a low firing temperature.

The components were selected based on the results of previous studies at the South-Russia State Technical University (NPI). The design matrix was in the  $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{TiO}_2 - \text{Na}_2\text{O} - \text{K}_2\text{O} - \text{Li}_2\text{O} - \text{CaO} - \text{P}_2\text{O}_5 - \text{NiO} - \text{Fe}_2\text{O}_3 - \text{MnO}_2 - \text{F}^-$  system and had the following chemical composition (mass content, %): 30.67  $\text{SiO}_2$ , 14.61  $\text{B}_2\text{O}_3$ , 2.88  $\text{Al}_2\text{O}_3$ , 16.77  $\text{TiO}_2$ , 17.19  $\text{Na}_2\text{O}$ , 7.08  $\text{K}_2\text{O}$ , 8.36  $\text{Li}_2\text{O}$ , 0.55  $\text{CaO}$ , 1.70  $\text{P}_2\text{O}_5$ , 0.075  $\text{NiO}$ , 0.075  $\text{Fe}_2\text{O}_3$ , 0.05  $\text{MnO}_2$ , 0.15  $\text{F}^-$ , and the remaining oxides were added over and above 100% (RF Patent No. 2247084). This frit can be used to manufacture a quality glass-enamel coating with CLTE,

chemical stability, whiteness, and gloss that satisfy the requirements of GOST 24788–2001.

Different coloring oxides and substances which color enamel different colors when they decompose were added (over and above 100%) to the batch to obtain single-coat colored glass enamels. The classification of the added dyes and properties of the synthesized frits are reported in Table 1.

Based on these studies, we selected the following frits for further developing the color range of the enamels:

for obtaining the dark-light-blue range: Nos. 1, 10, and 12;

for obtaining yellows: Nos. 2, 5, and 9;

for obtaining greens: Nos. 3 and 11;

for obtaining the red range: Nos. 4, 6, 7, 8, 13, and 14.

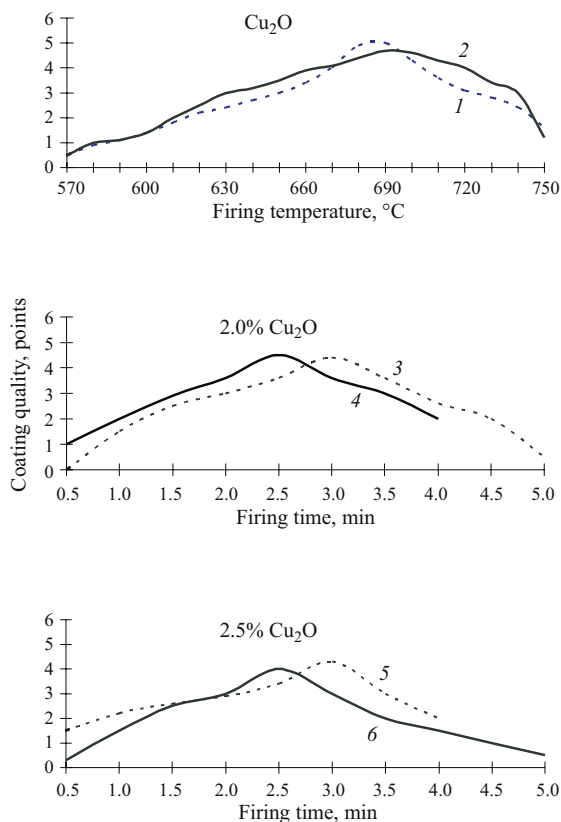
One of the fundamental conditions for formation of a continuous, strong, defect-free enamel coating on metals, especially a single-coat coating, is the appropriate preparation of their surfaces before applying the enamel [2]. The following method of preparing steel under single-coat enameling developed and patented at the South-Russia State Technical University is electrolytic copper plating (RF Patent No. 2248410), which consists of electrodeposition of a film of copper on the surface of the steel. This method is optimum for low-temperature, light, single-coat enameling in the 720–800°C firing temperature range. The highest adhesive strength (80%) is attained for a copper film thickness of 0.2  $\mu\text{m}$ , porosity of 11.0%, and roughness of  $R_z = 0.83 \mu\text{m}$ . Physicochemical methods of analysis showed that the presence of a copper film with the optimum thickness of 0.2  $\mu\text{m}$  on the steel causes formation of the crystalline phases  $\text{Fe}_2\text{SiO}_4$  and  $\text{Cu}_2\text{SiO}_4$  and  $\text{CuFe}_2\text{O}_4$  spinel in the contact layer on the metal–enamel boundary and ensures high adhesive strength of the steel–single-coat enamel composition together with the glass phase.

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TABLE 1

Frit No.	Coloring compound	Amount of substance added (over and above 100%), %	Color of synthesized frit	Degree of fusion*	Medium
1	CoO + Cu <sub>2</sub> O	0.5 + 0.5	Light blue	±	Oxidizing
2	NiO	2.0	Dark yellow	+	"
3	Cr <sub>2</sub> O <sub>3</sub> + Cu <sub>2</sub> O	1.0 + 1.0	Dark green	+	"
4	FeO	2.0	Brown	+	"
5	CeO <sub>2</sub>	3.5	Amber-brown	+	"
6	V <sub>2</sub> O <sub>5</sub>	2.0	Amber	+	"
7	V <sub>2</sub> O <sub>5</sub>	2.0	Light amber	+	Reducing
8	CdS	1.5	Amber-brown	+	Oxidizing
9	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.5	Lettuce-green	+	"
10	Cu <sub>2</sub> O	0.5, 1.0, 1.5, 2.0, 2.5, 3.0	Sky blue	+	"
11	CoO	0.5	Saturated violet	+	"
12	CoO + Cr <sub>2</sub> O <sub>3</sub>	0.25 + 0.25	Grey	±	Reducing
13	MnO <sub>2</sub>	0.5, 1.0, 2.0, 2.5, 3.0, 3.5	Bordeaux-brown	+	"
14	Sb <sub>2</sub> S <sub>5</sub>	2.0	Light brown	±	"

\* “+”) frit covers well, has satisfactory gloss, crystallization is not observed; “±”) frit has small embedded crystals, satisfactory gloss, and unsatisfactory covering; “-”) frit fuses poorly, contains sand crystals, has unsatisfactory gloss and covering, quality coatings not obtained from this frit.



**Fig. 1.** Coating quality as a function of the firing temperature-time range and amount of coloring oxide added: 1 and 2) 2.0 and 2.5% Cu<sub>2</sub>O; 3, 4, 5, and 6) 680, 690, 700, and 710°C.

These single-coat colored glass enamels are low-melting, with a firing temperature range within the limits of 670–740°C. The dependence of the quality of the coating on the firing temperature-time range and amount of coloring oxides added is demonstrated on the example of sky-blue enamels fabricated with addition of 2.0 and 2.5% Cu<sub>2</sub>O to the batch, over and above 100% (Fig 1).

The subsequent studies showed that the properties of the single-coat colored enamels obtained, such as chemical stability, adhesive strength, gloss, and thermal stability, satisfy the requirements of GOST 24788–2001.

The average values of the diffuse reflectivity (DR) — blue  $\rho_b$ , green  $\rho_g$ , and orange  $\rho_o$ , achromatic whiteness  $W_{ach}$ , coordinates of the three basic shades ( $X'$ ,  $Y'$ ,  $Z'$ ), coefficients of the three basic shades ( $X$ ,  $Y$ ,  $Z$ ), color brightness  $B$  (%), purity of hue  $P$  (%), and wavelength  $\lambda$  ( $\mu\text{m}$ ) were measured for the most promising single-coat enamels. The measurements of  $\rho_b$ ,  $\rho_g$ , and  $\rho_o$  were performed with a photoelectric sensor and the others were calculated with equations.

The following were calculated:

$$W_{ach} = -6.272\rho_b + 77.203\rho_g + 24.929\rho_o + 5.51;$$

$$X' = 1.723\rho_b + 33.383\rho_g + 70.688\rho_o + 1.98;$$

$$Y' = -6.273\rho_b + 77.20\rho_g + 24.929\rho_o + 2.51;$$

$$Z' = 35.108\rho_b - 1.079\rho_g - 0.243\rho_o + 0.85;$$

$X = X'/(X' + Y' + Z')$ , and  $Y$  and  $Z$  were calculated similarly.

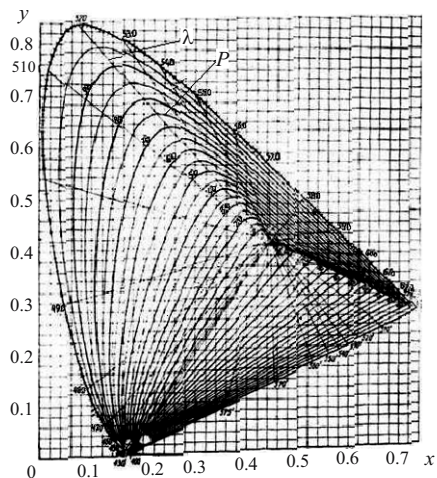


Fig. 2. MOK graph.

The colorimetric data for the coatings were calculated on the example of enamel containing 1.0%  $\text{MnO}_2$ . If  $\rho_b = 21\%$ ,  $\rho_g = 24\%$ , and  $\rho_o = 31\%$ , then  $X' = 3030.683$ ,  $Y' =$

$2496.416$ ,  $Z' = 704.83$ ,  $X = X'/(X' + Y' + Z') = 0.486$ ,  $Y = Y'/(X' + Y' + Z') = 0.701$ , and  $Z = Z'/(X' + Y' + Z') = 0.1131$ . The values of  $\lambda$  and  $P$  were determined with the MOK graph (Fig. 2),  $B = X$ .

The colorimetric data for the other synthesized coatings can be calculated similarly.

The colorimetric studies made it possible to plot spectral graphs and to create a concept of the position of this enamel in the color triangle, as well as how this position changes as a function of the amount of coloring compound added. The results obtained now allow theoretically determining what color the coating obtained will have.

## REFERENCES

1. *Technology of Enamel and Protective Coatings: A Textbook* [in Russian], Kharkov – Novocherkassk (2003).
2. E. A. Yatsenko, A. P. Zubekhin, and E. B. Klimenko, "Electrochemical methods of enhancing the adhesive strength of single-coat glass enamels with a metal substrate," *Steklo Keram.*, No. 3, 25 – 28 (2004).